

# Innovative Applications of Aqueous and Slow-Release Electron Donors: Two Case Studies

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## Introduction

Two case studies are presented that highlight innovative applications of bioremediation for cleanup of chlorinated solvents. In the first case study at the Idaho National Engineering and Environmental Laboratory's (INEEL's) Test Area North (TAN), an aqueous electron donor solution, sodium lactate, was used to facilitate reductive dechlorination of trichloroethene (TCE) in a residual source area in deep fractured basalt. This approach not only achieved complete dechlorination of TCE to ethene in the dissolved phase, it also accelerated dissolution of the residual TCE source. This facilitated an amendment to the site's Record of Decision replacing pump and treat with bioremediation in the source area. The second case study involves the challenging problem of a residual chlorinated solvent source area in a low permeability, variably-saturated medium. Funded by the National Science Foundation and EPA Region 4, a pilot study was performed to evaluate an innovative application of a slow-release electron donor. Chitin, the second most plentiful biopolymer in the world after cellulose, was injected into the low permeability medium via hydraulic fracturing. Chitin degradation resulted in the production of volatile fatty acids (VFAs) that facilitated reductive dechlorination throughout a significant volume of the low permeability formation. In fact, concentrations of all chlorinated aliphatic hydrocarbons (CAHs) decreased below regulatory limits in three of the five monitoring wells. In the remaining two wells, TCE decreased from a maximum concentration of 59 µg/L to 11 µg/L and cis-dichloroethene (cis-DCE) from a maximum of 450 µg/L to 99 µg/L. Both of these case studies are described in more detail below.

## Case Study 1 - TAN

**Background.** Historical waste disposal activities have resulted in a nearly 3-km-long trichloroethene (TCE) plume in the groundwater at the TAN facility of the INEEL. Facility process waste consisting of liquid organic, inorganic, and low-level radioactive waste along with sanitary sewage wastewater was injected directly into the Snake River Plain Aquifer (SRPA) via injection well TSF-05 from the mid-1950s to 1972. A 1995 Record of Decision (ROD) selected pump and treat as the default remediation technology with the provision to evaluate five innovative technologies, including enhanced bioremediation. Continuous pump and treat operations began in November 1996 and operated for approximately 18 months prior to preparing for the bioremediation field evaluation.

A field evaluation was conducted from November 1998 to September 1999 to determine whether anaerobic reductive dechlorination (ARD) of TCE could be enhanced through the addition of an electron donor (sodium lactate). A complete description of the operations and data generated during the field evaluation is presented in Sorenson (2000). Lactate injection began at well TSF-05 in January 1999. The injection strategy created electron donor concentrations in the thousands of milligrams per liter shortly after the initial injection. Following the 8-month Field Evaluation Phase, when lactate was injected weekly, concentrations of electron donor up to 4,500 mg/L were present in the aquifer treatment cell (Sorenson, 2000). At this time, lactate injections were discontinued for 5 months in order to (1) Determine the persistence of electron donor and ARD reactions within the treatment cell and (2) Evaluate the efficiency of ARD reactions in the prolonged presence of acetate, propionate, and butyrate (fermentation products) as electron donors. This period of time is referred to as Pre-

Design Phase I (PDP-I). Lactate injections were renewed once the electron donor in the treatment cell was depleted (~ 5 months later). The objective of this phase, referred to as Pre-Design Phase II (PDP-II), was to recreate the conditions that favored more efficient ARD in the absence of lactate injections during PDP-I by manipulating the lactate injection strategy.

## Materials and Methods

**Lactate Injection.** The strategy for lactate injection during the Field Evaluation Phase consisted of weekly injections, providing the system with a steady supply of electron donor. In PDP-II the goal was to provide a large mass of lactate on an infrequent basis. In order to achieve this, a mass of lactate corresponding to twice that of a single Field Evaluation Phase injection was injected every 8 weeks. The injection location was the same throughout the study.

**Monitoring Locations, Frequency, and Analytes.** The treatment cell consists of an injection well (Well TSF-05), an extraction well located approximately 150 m downgradient (Well TAN-29), and 11 monitoring locations (Figure 1). Groundwater monitoring was conducted at 8 locations on a biweekly basis and at all 11 locations on a monthly basis during the Field Evaluation Phase. Since that time all sampling has been monthly. Analytes consisted of electron donors, bioactivity indicators and nutrients, redox indicators, contaminants and degradation products, water quality indicators, and tritium, a co-contaminant that is used as a tracer.

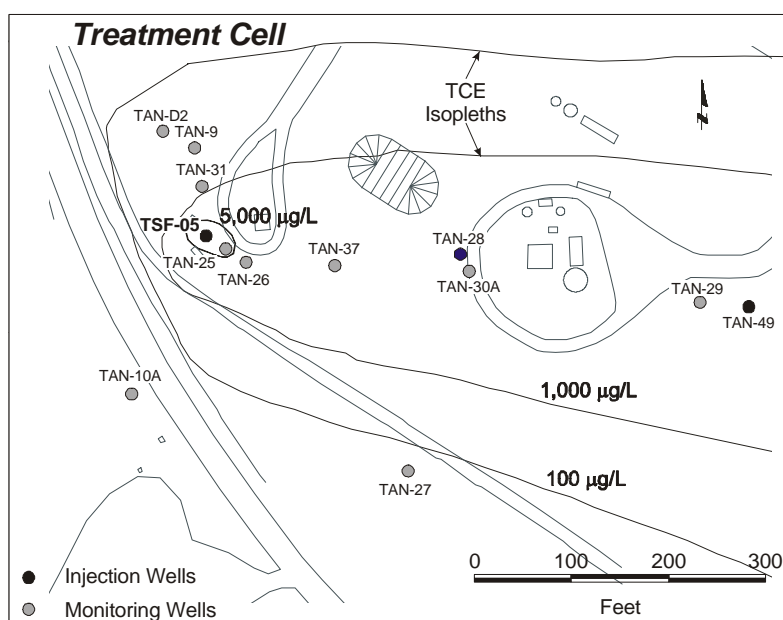


FIGURE 1. Bioremediation treatment cell.

## Results

Following rapid distribution of electron donor, the effect on redox conditions and ARD reactions was also rapid. Sulfate reduction began within 4 weeks of injection and methanogenic conditions were achieved within 5 months (Martin et al., 2001). ARD of TCE to cis-DCE began coincident with sulfate reduction in source area wells (Sorenson et al., 2000a). Complete ARD of cis-DCE to VC and ethene corresponded exactly to the onset of methanogenic conditions. An example of this is shown for monitoring well TAN-26 in Figure 2. Also apparent in Figure 2 is an initial significant increase of TCE concentrations. It was determined that the decreased interfacial tension between residual TCE and the electron donor solution accelerates mass transfer, leading to more rapid biodegradation (Sorenson, 2002). This is called Bioavailability Enhancement Technology™ (B.E.T.™).

Figure 3 shows the impact of almost 2 years of lactate injection on the distribution of contaminants in the treatment cell. After 18 months of pump and treat prior to lactate injection, TCE was present in the source area at concentrations greater than 3200 µg/L and downgradient at concentrations greater than 800 µg/L. After 2 years

of lactate addition, concentrations of TCE in the source area are below 5  $\mu\text{g/L}$ . Downgradient, the large area with concentrations greater than 800  $\mu\text{g/L}$  initially present is greatly reduced in size and the maximum concentration has been reduced by half to around 400  $\mu\text{g/L}$ . This bioremediation effort has been extremely successful compared to the pump and treat remedy. However, a zone of relatively high TCE concentrations remains immediately downgradient of the source area. The lactate addition strategy employed during PDP-II does not appear to be completely effective in impacting the full extent of the source area as observed during PDP-I (Sorenson et al., 2000b). This will be resolved during long-term operations.

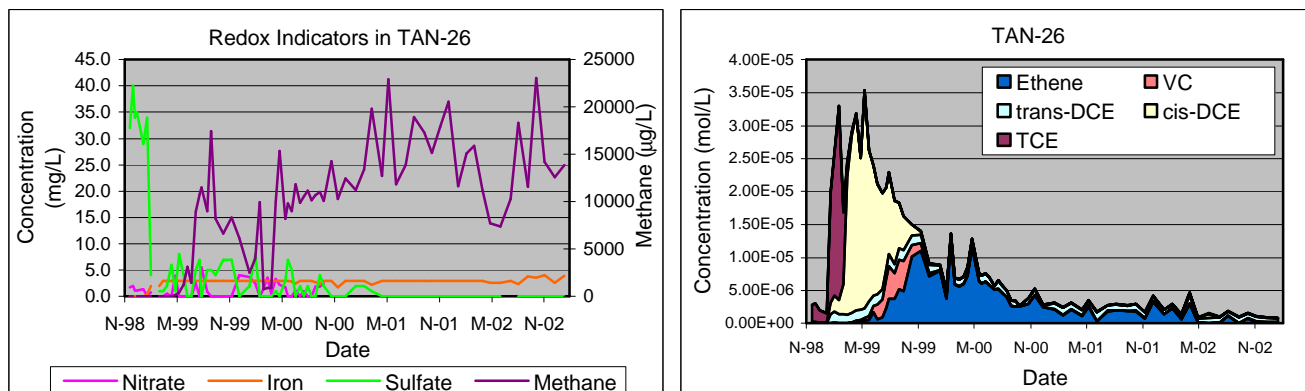


FIGURE 2. Redox indicators and dechlorination.

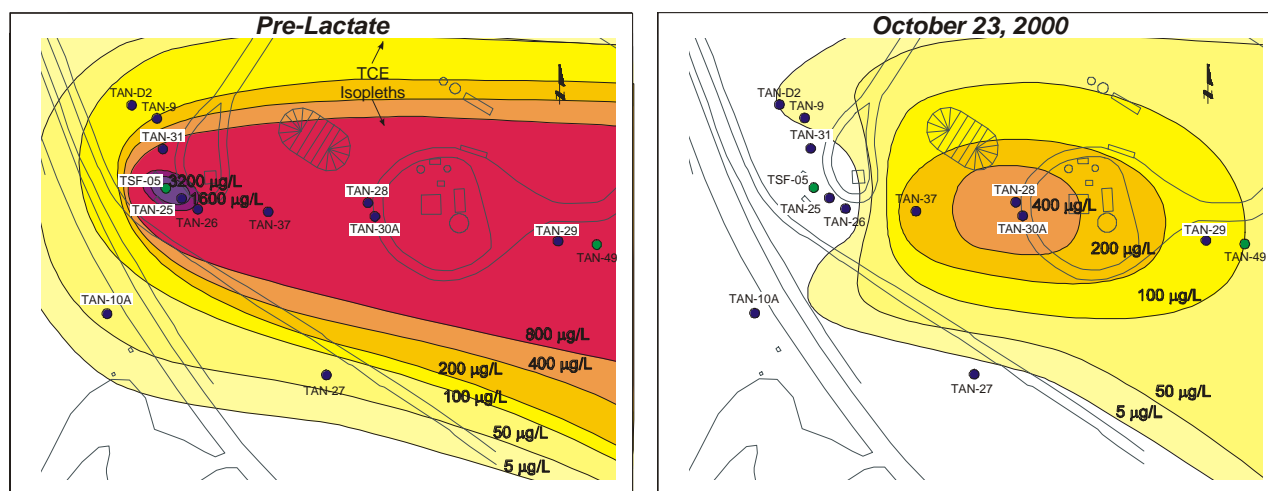


FIGURE 3. Effect of lactate addition on TCE source area (after Martin et al., 2001).

## Conclusions

The bioremediation field test conducted at TAN has been extremely successful compared to the default pump and treat remedy (Figure 3). This has resulted in a ROD Amendment replacing pump and treat with bioremediation in the source area. Results collected to date indicate that the system can be further manipulated to achieve more efficient ARD of TCE throughout the entire source area. In order to achieve this, additional lactate injection strategies, including a new location, are being considered to achieve a better distribution of electron donor. In particular, a location near well TAN-37 could be utilized as an injection location in order to distribute electron donor within the downgradient portion of the source area.

## Case Study 2 – Distler Brickyard

**Background.** The National Science Foundation sponsored a pilot-scale field test of enhanced bioremediation at the Distler Brickyard site near Louisville, KY, from October 2001 to January 2002. The pilot test technology combined the use of hydraulic fracturing ("fracing") with anaerobic bioremediation enhanced by the addition of chitin, a solid, natural polymeric organic material consisting of shrimp and crab shells. The primary objectives of the field test were to determine if fracing would enhance the geologic formation's permeability and if the addition

of chitin would impact the aquifer's geochemistry in ways conducive to anaerobic reductive dechlorination (ARD). Field data indicate that active ARD of trichloroethene (TCE) continues to occur in the treatment area as a result of chitin/fracing.

Groundwater at the Distler Brickyard site contains TCE and cis-DCE at concentrations reaching nearly 100 and 500 µg/L, respectively. The underlying stratigraphy consists of approximately 40 ft of silty-sand and silty-clay overlaying shale bedrock. The groundwater table is approximately 30 ft below ground surface (bgs). Horizontal hydraulic conductivities range from  $10^{-8}$  to  $10^{-4}$  cm/sec. Although monitoring data indicate that natural biodegradation via ARD was occurring, the rate and extent of ARD reactions are limited by a lack of sufficient electron donor and the low permeability of the formation. Earlier laboratory studies conducted by the University of Illinois at Urbana/Champaign (UIUC) demonstrated that chitin produces volatile fatty acids (VFAs) shown to be high-quality electron donors for ARD.

## Materials and Methods

Hydraulic fracturing was conducted at the Distler Brickyard through a single borehole within the contaminant source area, near the bedrock surface. By injecting sand slurry with chitin, three sets of highly permeable fractures were created in the borehole at depths of 25, 33, and 38 ft bgs. Approximately 250 gallons of the (1:4 ratio) chitin/sand slurry were delivered into each frac. The borehole subsequently was completed as a monitoring well. The hydrologic system evaluation included tiltmeter monitoring to measure the orientation of fractures, pre- and post-fracing slug tests, and a pumping test.

Ground-water sampling in the fracing well and surrounding monitoring wells was conducted to determine the effect of chitin emplacement on the electron donor concentrations, oxidation-reduction (redox) conditions, and ARD. The breakdown of chitin as an electron donor was measured by the production of individual VFAs such as acetate, propionate, isobutyrate, butyrate, isovalerate, and formate. Monitoring was conducted five times during the 9 months after injection at five monitoring wells.

## Results

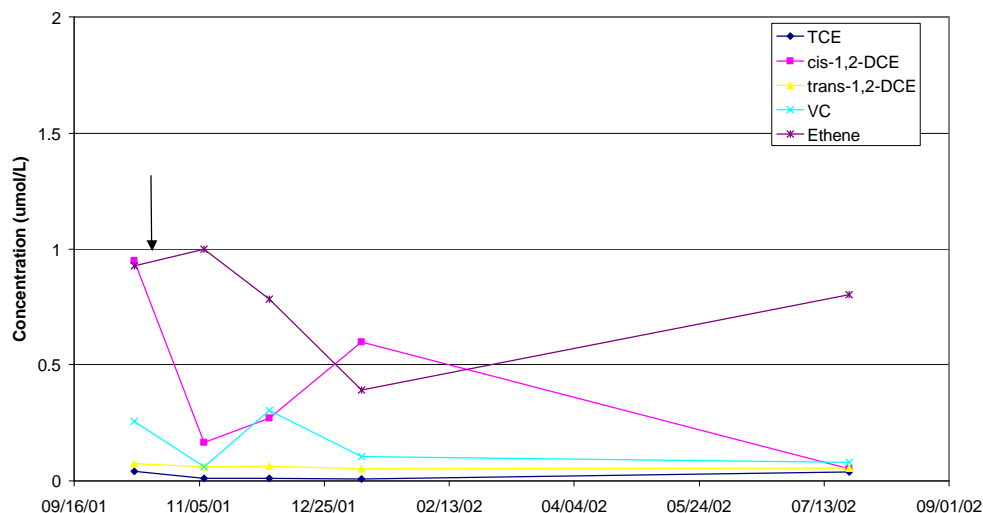
Results indicated that fracing produced a network of three permeable zones with a modeled effective radius of 4 ft for the uppermost frac (within the silt/sand unit) and 13 ft for the two lower fracs (within the silt/clay unit) (Martin et al. 2002). As anticipated, the extent of fracture propagation depended upon the site's lithology, degree of soil consolidation, presence and orientation of bedding planes, and presence of geologic heterogeneities. Despite the heterogenous propagation of fractures, the pumping test showed that all four of the monitoring wells were in direct hydraulic connection with the fracing well.

Monitoring well data showed that the dominant VFAs produced from chitin were acetate and butyrate, which reached maximum concentrations of greater than 600 and 300 mg/L, respectively. Acetate concentrations of greater than 200 mg/L persisted in the treatment cell 9 months following chitin emplacement. Conditions became more reducing following chitin emplacement. Redox conditions were assessed using concentrations of ferrous iron, sulfate, and methane. Strong methanogenic conditions, which are required for successful ARD, were indicated by the increased concentrations of methane and ferrous iron and by the absence of sulfate. Ferrous iron concentrations increased and sulfate dropped within the first month after chitin emplacement, indicating an immediate impact to redox conditions. Methane concentrations began increasing steadily approximately two months after chitin emplacement and reached up to 12,000 µg/L within nine months.

Concentrations of TCE and breakdown products cis-1,2-DCE, vinyl chloride, and ethene were monitored to further evaluate the ARD process (Figure 4). Data indicated an initial decrease in *cis*-1,2-DCE following chitin emplacement, followed by a three-month rebound. In contrast, ethene concentrations initially increased but subsequently decreased. (These trends may be attributed to higher groundwater levels and dilution effects.) After nine months, however, *cis*-1,2-DCE concentrations dropped below detection (5 µg/L), and a nearly stoichiometric increase in ethene concentrations was observed.

## Conclusions

These results indicate the persistence of ARD reactions as long as nine months after chitin emplacement. Overall concentrations of chloroethene contaminants in the source area decreased to or below maximum contaminant levels (MCLs) in three of the five wells within nine months. Full-scale application of chitin/fracing technology at the Distler Brickyard during 2003 will focus on evaluating the technology's cost-effectiveness, achieving adequate distribution of chitin in-situ, and evaluating the long-term performance of chitin as a slow-release electron donor for ARD of chloroethene contaminants in low-permeability systems.



**FIGURE 4. Dechlorination due to chitin injection in a low-permeability system.**

## References

- Martin, J. P., K. S. Sorenson, and L. N. Peterson, 2001. "Favoring Efficient In Situ TCE Dechlorination through Amendment Injection Strategy." *Anaerobic Degradation of Chlorinated Solvents*, V. Magar, D. Fennell, J. L. Morse, B. Alleman, and A. Leeson eds., Battelle Press, Columbus, OH, pp. 265-272.
- Martin, J. P., K. S. Sorenson, L. N. Peterson, R. A. Brennan, C. J. Werth, R. A. Sanford, G. H. Bures, and C. J. Taylor, 2002. "Enhanced CAH Dechlorination in a Low-Permeability, Variably Saturated Medium." In: *Remediation of Chlorinated and Recalcitrant Compounds – 2002 Proceedings of the Third International Conference*, A. R. Gavaskar and A. S. C. Chen, eds., Battelle Press, Columbus, OH.
- Sorenson, K. S. 2000. *Intrinsic and Enhanced in situ Biodegradation of Trichloroethene in a Deep, Fractured Basalt Aquifer*. Ph.D. Dissertation. University of Idaho, Idaho Falls, ID.
- Sorenson, K. S., L. N. Peterson, and R. L. Ely, 2000a. "In Situ Biostimulation of Reductive Dehalogenation – Dependence on Redox Conditions and Electron Donor Distribution." *Groundwater 2000*, P. L. Bjerg, P. Engesgaard, and Th. D. Krom, eds., A. A. Balkema Publishers, Rotterdam, Netherlands, pp. 379-380.
- Sorenson, K. S., L. N. Peterson, and R. L. Ely, 2000b. "Enhanced In Situ Bioremediation of a TCE Source Area in Deep, Fractured Rock." *Contaminated Site Remediation: From Source Zones to Ecosystems*, Proceedings of the 2000 Contaminated Site Remediation Conference, C. D. Johnston ed., Centre for Groundwater Studies, Wembley W. A., Australia, pp. 621-628.
- Sorenson, K. S., 2002. "Enhanced Bioremediation for Treatment of Chlorinated Solvent Residual Source Areas." In: *Innovative Strategies for the Remediation of Chlorinated Solvents and DNAPLS in the Subsurface*, S. M. Henry and S. D. Warner eds., ACS Symposium Series 837, ACS Books, Washington, D.C., pp. 119-131.